1917
H85

Hsun

The Methods of Analysis of Non-Ferrous Alloys—
The Purification of Precipitated Metastannic Acid

THE METHODS OF ANALYSIS OF NON-FERROUS ALLOYS—THE PURIFICATION OF PRECIPITATED METASTANNIC ACID

BY

JIN JEE HSUN

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMISTRY

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1917

1917
H85

UNIVERSITY OF ILLINOIS

May 29th 1917

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Jin Jee Hsun

ENTITLED THE METHODS OF ANALYSIS OF NON-FERROUS ALLOYS -

THE PURIFICATION OF PRECIPITATED METASTANNIC ACID.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemistry

T. R. Ball.
Instructor in Charge

APPROVED: W. A. Noyes

HEAD OF DEPARTMENT OF CHEMISTRY.

9 Feb 17 Culley

370558

TABLE OF CONTENTS

		Page
I.	OBJECT OF INVESTIGATION----------	1
II.	THEORIES OF OCCLUSION----------	2
III.	METHODS OF AVOIDING THE ERRORS OF OCCLUSION-------	4
IV.	METHODS OF PURIFYING METASTANNIC ACID----------	5
V.	EXPERIMENTAL----------	8
VI.	EXPERIMENTAL DATA----------	10
VII.	SUMMARY----------	13

THE METHOD OF ANALYSIS OF NON-FERROUS ALLOYS-
THE PURIFICATION OF PRECIPITATED METASTANNIC ACID

I. OBJECT OF THE INVESTIGATION

In the analysis of alloys containing tin, this metal is always brought down by dilute nitric acid in the form of metastannic acid which is ignited into stannic oxide and weighed; the percentage of tin is calculated from the oxide formula. Although the electrolytic method is the most accurate, it requires elaborate apparatus which is often not available to analysts who analyze this kind of an alloy occasionally. The property of metastannic acid to occlude many metals, especially iron, lead, copper, zinc, and manganese - probably owing to the formation of insoluble salts of metastannic acid - often causes much trouble, and when the percentage of tin in the alloy is large, these occlusions must be completely removed and collected; otherwise, the subsequent determinations of both tin and other components of the alloy can not be expected to reach any high degree of accuracy. Hence a short and simple method of removing the occlusions from metastannic acid is desirable.

Digitized by the Internet Archive
in 2013

http://archive.org/details/methodsofanalysi00hsun

II. THEORIES OF OCCLUSION

The exact nature of occlusion is at present an open question. Schneider* suggests that the soluble salt is taken up by the precipitate as the latter separates and is distributed throughout the interior of the precipitate; that is, it is a solid solution in which the precipitate is the solvent and the soluble salt the solute. If this view is correct, there should be a definite saturation limit for every precipitate with respect to every occluded substance; but such limits have not been found in most cases investigated.

Ostwald# concludes that an attractive force is exerted by the precipitate to hold the dissolved substance in the neighborhood of its boundary surfaces, thus either delaying or preventing the removal of these substances by washing. He designates this phenomenon as "adsorption", by which he means the retention of soluble substance by finely divided particles when placed in the solution containing them. A typical example is the adsorption of coloring matter by bone-charcoal from solution. But very few precipitates adsorb coloring matter, and their ability to retain soluble salts is of a decidedly selective character.

Richards+ thinks that this phenomenon is due to chemical force rather than to physical force. He designated

---

*E. A. Schneider, Zeit. Physik. Chem., Vol. 10, p. 423, (1892).

#W. Ostwald, Grundriss der Allgemeinen Chemie, p. 338, (1899).

+T. W. Richards, Proc. Am. Acad. of Science, Vol. 35, pp. 377-383, (1900).

it as "occlusion". His theory suggests that some slightly soluble basic salts or molecular compounds are formed with the precipitate. For instance, the occlusions of ferric salt by barium sulphate may be due to the fact that the latter is contaminated with a small amount of double sulphate of the formula $BaSO_4 \cdot Fe_2(SO_4)_3 \cdot H_2O$. This compound, when ignited, is changed into $BaSO_4$ and Fe_2O_3 which therefore gives low results for sulphur. The experiments of Hulett and Duschak* on the occlusion of potassium nitrate by barium sulphate also indicate the probable formation of compounds of the type $BaSO_4.Ba(NO_3)_2$ or $Ba_2(NO_3)_2SO_4$.

While any one of the theories mentioned might apply to the occlusion of metals by metastannic acid, the acidic nature of the precipitate makes it seem reasonable that the occlusion might be due to the formation of difficulty soluble salts of the acid, e. g., $M\ddot{e}SnO_3$ or $M\ddot{e}(HSnO_3)_2$.

---

*Hulett and Duschak, Zeit. für Anorg. Chemie, Vol. 40, p. 196, (1904).

III. METHODS OF AVOIDING THE ERRORS OF OCCLUSION

When the ion in question is occluded only slightly by the precipitate, the error from this source can be reduced to an almost neglible amount by making the precipitation in a sufficiently dilute solution. In some cases, it is easier to repress the degree of ionization of the occluded substance by adding some reagent which forms a complex ion with it; in other cases, it is necessary to make a double precipitation. All of these methods take advantage of the fact that the amount of occlusion decreases as the concentration of the occluded ion in the solution from which the precipitate separates decreases, although it is not proportional to the concentration. In a few cases it is possible to replace the occluded ion by another ion which can be converted into a gas or which is occluded to a smaller extent.

IV. METHODS OF PURIFYING METASTANNIC ACID

Doctor Busse* recommended two methods as follows:

(a) The contaminated metastannic acid is ignited to stannic oxide which is decomposed by fusing with six times its weight of a mixture of equal parts of calcined sodium carbonate and pure sulphur. The melt is treated with hot water whereby tin goes into solution as sodium thiostannate. The brown liquid containing all of the tin and some of the occluded metals is treated with sodium sulphite to destroy the sodium polysulphide, in which copper and iron sulphides are somewhat soluble. When the liquid becomes only slightly yellow in color, the impurities precipitate out as sulphides which are separated by filtration from the pure sodium thiostannate. The latter salt, upon adding a slight excessive of acetic acid, is converted into stannic sulphide which is ignited to pure stannic oxide.

This method, in the hands of an experienced analyst, is accurate, but it is by no means simple and short; for the process of fusion not only requires time, but is a disagreeable one to carry out. Moreover, two fusions are generally required to get all of the tin into solution. This method, therefore, is not generally recommended by teachers.

(b) The contaminated metastannic acid is treated with 1 cc of pure sodium hydroxide and 10-15 cc of concentrated sodium sulphide solution. It is then heated on the water bath until the tin goes into solution as sodium thiostannate.

---

*E. Busse, Zeit. für Anal. Chem., Vol. 17, p. 53, (1878).

The other metals precipitate out as sulphides which are removed by filtration. The precipitate, with the filter paper, is again treated with sodium sulphide solution for 30 minutes to insure the complete extraction of tin. The two combined filtrates contain the pure sodium thiostannate which is converted into stannic oxide in the same manner as was described under (a) above.

This method, while more simple than the first, does not eliminate the chief cause of error. When the thiostannate solution is acidified, the precipitated stannic sulphide carries down sodium salt which can not be removed by washing.* This error arises in both methods.

Some authors recommended the use of ammonium sulphide, but this reagent dissolves a slight amount of copper which will precipitate out as cupric sulphide with the stannic sulphide upon the addition of acetic acid. This sulphide not only increases the weight of stannic oxide, but is also a source of error in the subsequent determination of copper. The process is also slow and uncertain.

The method recommended by Doctor Oettel+ for removing phosphorous from stannic oxide can not be applied to free the tin from occluded metals. He fuses contaminated stannic oxide with three times its weight of potassium cyanide, whereby tin is reduced to the metallic form, while phosphorous is converted into potassium phosphate. But potassium cyanide reduces, besides tin, many occluded metals. For instance, the occluded copper and lead would be reduced even before the tin

*F. Henz, Zeit. Anorg. Chem., Vol. 37, p. 39, (1903).
+F. Oettel, Chemiker Zeitung, P. 19 (1896).

itself. In a fused condition, they would form an alloy so that no purification from occluded copper and lead would result.

In view of the above difficulties, a new method has been sought for the purification of metastannic acid, which would be more certain to yield good result in the hands of beginning students, and if possible, one that would require less time.

All of the available methods depend upon the separation of tin from the occluded metals by putting it into solution. If a method could be gotten to "open up" the contaminated precipitate so that it could be attacked by nitric acid and the metastannic acid thrown out again in the presence of a small amount of other metals, the precipitate should be practically pure. In order to accomplish this, the reagent used must be one which forms a compound with copper and lead which is less soluble than the ones in which they exist in the precipitate, or one which may be added in sufficiently high concentration to effect the change into other compounds by mass action. It must be either readily removed from the solution or be of such a nature that if it is occluded, it would be volatilized when the metastannic acid is ignited. Since hydrogen sulphide forms exceedingly insoluble sulphides with the metals in question, readily decomposed with nitric acid, and can be removed from solution, its use is at once suggested.

V. EXPERIMENTAL

The purest tin available was fused with potassium cyanide in order to remove any oxide. Portions were then cut off with a knife, converted into metastannic acid with nitric acid, and the precipitate ignited to stannic oxide. No process of purification of stannic oxide was thought necessary, because of the small amount of impurity which must have been present when the metastannic acid was precipitated. The following data will show that the tin was sufficiently pure to serve as a standard in the determinations which follow:

Wt. of Sn Taken	Wt. of Sn Calc. from SnO_2	% Purity
.4286 Gram	.4284 Gram	99.95
.4940 "	.4940 "	100.00
	Mean =	99.97

Accurately weighed quantities of the pure tin were placed in a casserole and standard lead, copper and zinc nitrate solutions, containing the weights of metals given in their respective columns in the table, were added, together with 25 cc of nitric acid (sp. g. 1.20). The solution was heated on the water bath to complete dryness, the residue moistened with 5 cc of dilute nitric acid (Sp. G. 1.20) and then 50 cc of boiling distilled water was added. The solution was filtered hot; if the liquid cools, the metastannic acid becomes partly soluble. If the filtrate was hazy, it was refiltered until it became perfectly clear. After washing, the precipitate with the filter

paper was put into a 100 cc Erlenmeyer flask containing 50 cc of water which had just been boiled to expel all of the air. The flask was immediately connected to a hydrogen sulphide generator. Almost instantly, a black precipitate was observed in the flask, showing a conversion of the occluded metals into sulphides. This procedure takes advantage of Henry's Law, which states that the mass of gas dissolved by a given mass of solvent is directly proportional to the pressure, provided no chemical combination takes place between the gas and the solvent. Now if the water in the Erlenmeyer flask is boiled, it drives out the air,- when it cools and condenses in an atmosphere of hydrogen sulphide, the partial pressure of hydrogen sulphide in the flask will be high just in proportion as the partial pressure of air in it is low. This treatment is certainly more effective than the use of hydrogen sulphide water, which has been saturated in contact with air; for the hydrogen sulphide is escaping into the air all the time.

After this reaction was completed, the Erlenmeyer flask was detached from the generator. The whole material in the flask was transferred to the original casserole, the hydrogen sulphide in it was boiled out, enough dilute nitric acid was added to dissolve all the sulphides and the excess of nitric acid was neutralized with ammonium hydroxide (methyl orange). The metastannic acid thus produced was perfectly white; it was filtered, washed with one per cent ammonium nitrate solution, and ignited to stannic oxide. The percentage of tin was calculated from the oxide formula.

VI. EXPERIMENTAL DATA

Table I contains the data obtained by the above procedure with synthetic sample containing a total of approximately one gram of metal. The copper ranges from .62 to .70 gr; the lead from .21 to .15. The amount of lead and tin present is more than would usually be found in a brass, but this large amount was taken to increase the amount of occlusion as much as possible. 0.0788 gr. of zinc was present in each case. The 50 cc of water in the flask containing the contaminated metastannic acid was cooled in ice water during the 60 minutes it was being treated with hydrogen sulphide.

TABLE I.

Final Temp. of Saturation.	Time of H_2S treatment in Min.	Grams of Metals taken Cu	Pb	Zn	Sn	* Wt. of Sn. found	Error
0° C	60	.70	.15	.0788	.0733	.0730	-0003
"	60	.70	.15	"	.0720	.0721	+0001
"	60	.66	.17	"	.0730	.0735	+0003
"	60	.66	.17	"	.0707	.0715	+0004
"	60	.64	.19	"	.0730	.0737	+0007
"	60	.64	.19	"	.0722	.0725	+0003
"	60	.62	.21	"	.0727	.0735	-0002
"	60	.62	.21	"	.0717	.0717	-0003
						Mean =	+0002

A study of the last three columns shows that the amount of occluded metals is very small indeed. In eight

*The original volume of the solution was 43 - 47 cc.

determinations, the mean amount of tin recovered was within 0.0002 gr. of the amount taken. The ignited stannic oxide had a very slight yellowish color in each case.

In order to determine the effect of the time of hydrogen sulphide treatment, the experiments tabulated in Table II were made.

TABLE II

Final Temp. of Saturation.	Time of H_2S treatment in Min.	Grams of Metals taken Cu	Pb	Zn	Sn	* Wt. of Sn. found	Error
0° C.	60	.80	.07	.10	.0702	.0699	-.0003
"	60	.55	.07	.20	.0719	.0725	+.0006
Room Temp.	60	.80	.07	.10	.0723	.0716	-.0007
" "	60	.55	.07	.20	.0700	.0706	+.0006
Temp. not taken	30	.80	.07	.10	.0712	.0721	+.0009
" " "	30	.55	.07	.20	.0706	.0709	+.0003
" " "	15	.80	.07	.10	.0713	.0718	+.0005
" " "	15	.55	.07	.20	.0741	.0742	+.0001
" " "	10	.80	.07	.10	.0738	.0734	-.0004
" " "	10	.55	.07	.20	.0705	.0700	-.0005
" " "	5	.80	.07	.10	.0715	.0702	-.0013
" " "	5	.55	.07	.20	.0702	.0700	-.0002
						Mean =	+.00005

From the above table, it can be seen that the metastannic acid can be purified by suspending it in boiling water and treating with hydrogen sulphide for 5 minutes. However, to insure complete transformation in every case, 30 minutes will be recommended.

Synthetic tin-lead samples were prepared approximating

*The original volume of the solution was 38 - 44 cc.

the composition of solder by adding standard lead nitrate to weighed quantities of tin. This method of purification was applied to the tin component of this mixture with the following results:

TABLE III.

Final Temp. of Saturation.	Time of H_2S treatment in Min.	Grams of Metals taken Pb	Sn	Wt. of Sn. found	Error
Room Temp.	30	.1500	.1005	.0986	-.0009
"	30	.1500	.1000	.0999	-.0001
"	30	.1200	.1200	.1197	-.0003
"	30	.1200	.1206	.1200	-.0006
"	30	.1200	.1006	.1006	±.0000
"	30	.1200	.1000	.0999	-.0001
"	30	.1000	.1000	.0981	(-.0019)
"	30	.1000	.1000	.0994	-.0006
				Average	-.0004

From the data of Table III, it is evident that this method can be applied to the determination of tin in solders as well as in brass. However, special care should be taken in filtering metastannic acid derived from lead-tin alloys, since it is very liable to go through the filter paper, and be lost in the filtrate. If the filtrate looks hazy, 20 cc of one per cent ammonium nitrate must be added, the solution heated, and filtered again.

To further verify the accuracy of this method, a brass which was known to contain 7.00 % of tin was analyzed. Two analyses showed 7.10% and 7.12% respectively.

*The original volume of the solution was 31 - 33 cc.

VII. SUMMARY

Since the existing methods for the purification of metastannic acid, obtained in the analysis of tin bearing alloys, are difficult to carry out, and are therefore inaccurate in the hands of beginning students in quantitative analysis, a simpler and more accurate method has been sought. By treating the impure metastannic acid with a solution of hydrogen sulphide saturated under approximately one atmosphere's pressure for 30 minutes, the lead, copper and zinc which it contains may be readily put into solution with nitric acid, after expulsion of the excess of hydrogen sulphide by evaporation. Upon reconverting the tin into metastannic acid in the presence of this small amount of copper, lead, and zinc, a precipitate is obtained which is practically free from occluded metals. The method is easy to carry out and has a decided advantage over the previously used methods in that one treatment effects the purification, whereas the other methods require two or even three treatments.

UNIVERSITY OF ILLINOIS-URBANA
3 0112 082199180